SYNLETT

Spotlight 457

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

6-Diphenylphosphinopyridin-2-(1*H*)-one (6-DPPon)

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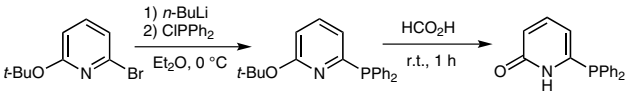
Dedicated with best wishes to Prof. Dr. Bernhard Breit at Albert-Ludwigs-Universität Freiburg

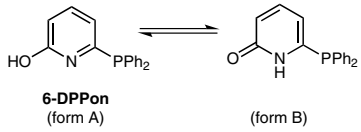
Introduction

Among heterocyclic structural units, pyridines are the most prevalent and have attracted the attention of chemists.[1] One important aspect of pyridine chemistry is designing new ligands based on the pyridine core.[2] Inspired by DNA base pairing, 6-DPPon (white solid, mp: 187 °C) was introduced by Bernhard Breit (Albert-Ludwigs-Universität Freiburg) as a monodentate ligand.[3] This compound can not only be easily prepared (Scheme 1) but also has a brilliant property: the ability for self-assembly.[4]



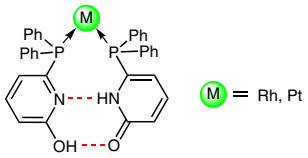
Scheme 1 Preparation of 6-DPPon

6-DPPon has two tautomeric forms, a 2-pyridone and a 2-hydroxypyridine tautomer (Scheme 2).



Scheme 2 Tautomeric forms of 6-DPPon

Interaction between form A and form B through hydrogen bonding can in situ generate a bidentate donor ligand in the coordination sphere of a metal (rhodium and platinum) center (Scheme 3). The present subject can open new gates to the design of self-assembled ligands and can be considered in related chemistries.

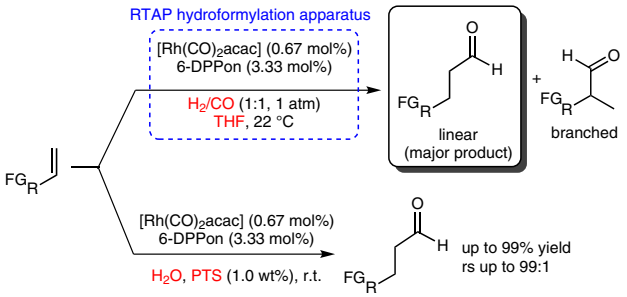


Scheme 3 Self-assembly of the 6-DPPon ligand

Abstracts

(A) *Room Temperature Ambient Pressure (RTAP) Hydroformylation of Terminal Alkenes*

Breit and co-workers have developed a hydroformylation of terminal alkenes under mild conditions: at room temperature and under ambient pressure. A bidentate donor ligand, generated in situ by self-assembly of 6-DPPon, reacted with rhodium and created a new catalyst with unique properties. Various ligands were tested in comparison to 6-DPPon and the best results (high yield and little isomerization) were obtained with 6-DPPon. High selectivity, low catalyst loading, a high level of generality, and excellent reactivity were some promising aspects of this protocol.[5] It was found that terminal alkenes can be hydroformylated in aqueous media by slightly changing the reaction conditions. Breit and co-workers investigated various surfactants, and the results indicated that polyoxyethanyl-α-tocopheryl sebacate (PTS) was the best choice. Interestingly, 6-DPPon was the best ligand for this reaction. It is worth noting that in addition to the advantages described above, with the new protocol the structure of the self-assembly catalyst is stable in water as a protic solvent; an important point for self-assembled structures.[6]



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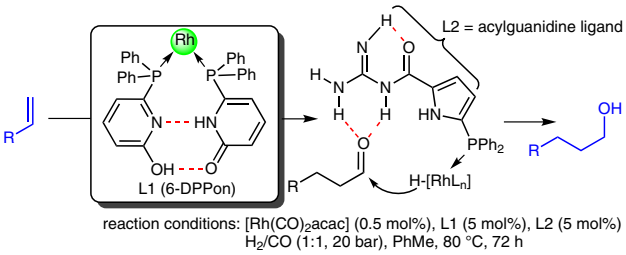
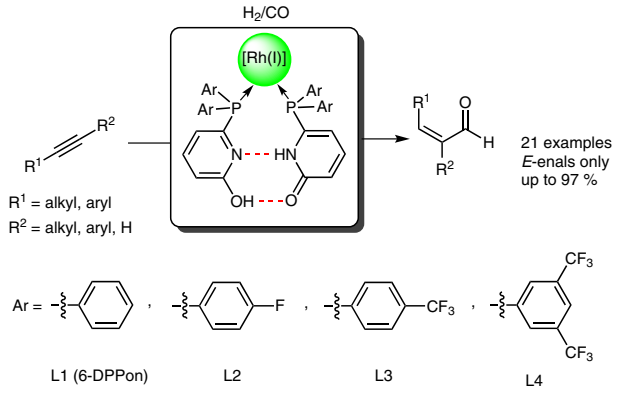
(B) *Tandem Rhodium-Catalyzed Hydroformylation–Hydrogenation of Alkenes*

In 2012, a unique tandem reaction was designed. In this reaction, a one-pot conversion of alkenes into linear alcohols is achieved using two different transformations (hydroformylation of alkenes and aldehyde hydrogenation). The first step (hydroformylation) was mediated by a rhodium complex which was generated by coordination of two 6-DPPon's, and a second step was carried out with an acylguanidine ligand. High regioselectivity and simultaneous a highly chemoselective reduction were two highlights of this work.[7]



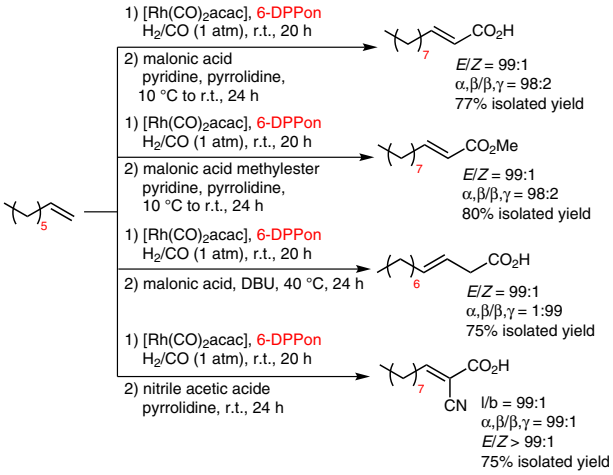
(C) *Hydroformylation of Alkynes*

Alkynes were hydroformylated stereo- and chemoselectively using 6-DPPon as a self-assembling ligand. In this study, several derivatives of the mentioned ligand were designed and investigated. This was the first time that dialkyl- as well as diaryl-substituted alkynes furnished *E*-enals with excellent chemo- and stereoselectivity.[8]



(D) *One-Pot C3-Homologation of Terminal Alkenes*

A new method to furnish carbonyl and carboxylic compounds was established by Breit and co-workers. In this method, by a combination of regioselective RTAP hydroformylation with 6-DPPon and a rhodium catalyst followed by decarboxylative Knoevenagel reaction (organocatalysis), various interesting compounds were produced.[9] In all of the reactions, the presence of 6-DPPon was crucial.



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